The study of concentration structural fluctuations in aqueous solutions of carboxylic acids and dimethylformamide by Rayleigh light scattering.

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Abstract. The results of Rayleigh isotropic light scattering in aqueous solutions of trichloro-acetic, acetic, propionic, butyric acids and dimethylformamide were presented. The scattering intensity narrow maxima were observed for all studied binary mixtures at 0.02-0.12 mole fractions of these compounds in water. With temperature increasing these maxima fall down. For elucidation of these maxima nature were also studied C=O vibrations band Raman spectra of these mixtures dissolved compounds. In pure liquids for C=O vibrations of acids correspond the three overlapping bands with different depolarization ratios, which correspond to various aggregated formations, from which are most stable the closed dimmer formations which do not destroy even at strong dilution of acids in neutral solvents. In aqueous solution at small content of acids for C=O vibrations corresponds a single band. As was to be expected the structural changes in mixture do not essential affect on C=O vibrations band. Obtained results were explained by structural fluctuations of concentration arising due to hydrate clatrates formation in this mole fractions interval of concentrations. Results of Raman scattering spectra in these acids+water solutions confirm this supposition.

Introduction. The Rayleigh isotropic light scattering in pure liquids is caused by density fluctuations in dimensions is smaller than wavelength of light. In solutions the considerable contribution to isotropic scattering give the concentration fluctuations. The thermodynamic calculations of these fluctuations for linearly polarized falling on the mixture light, at 90^0 scattering geometry, gives for concentrational scattering coefficient R_c the following expression [1]:

$$R_c = \frac{\pi^2}{\lambda^4 N_A} \cdot (2n \frac{dn}{dx_1})^2 \cdot x_1 \cdot x_2 \cdot V_M \cdot f \quad (1)$$

were λ is wavelength of light, N_A is Avogadro constant, n is refractive index of solution, x_1 and x_2 are mole fraction of solution components, f is concentration fluctuations function depending from thermodynamic properties of solution and characterizing the deviation of solution behavior from ideality. Therefore by the measurement of R_c one can try about the thermodynamic properties of solution. If f =1 then solution is ideal, if $f \succ 1$ or $f \prec 1$, then solution displays the positive or negative deviations from ideality, respectively. Now the light scattering method widely use for determination of various parameters of solutions [1-4].

Isotropic light scattering in aqueous solutions has peculiarity, in most cases side by side with usual concentrational light scattering arises the additional light scattering maximum at low concentrations (0.02-0.15 mole fr.) of organic compound. This maximum is especially clearly displayed in binary mixtures of alcohols with water [1]. The concentrational fluctuations caused this additional maximum by authors studied them were called as structural fluctuations of concentration, which according [1,5] are similar to fluctuations taking place at second type phase transitions (in that sense that the first take place at narrow concentration interval, second at narrow temperature interval), and caused by the destruction of local friable water structure after the filling of this structure cavities by dissolved molecules. These rebuildings of water local structure lead to large fluctuations of concentration. Although in this field of research a considerable experimental data were accumulated the perfect notion is still absent. Therefore the search of new aqueous systems with such structural fluctuations of concentration represents scientific interest.

In work [6] were studied Rayleigh light scattering in aqueous solutions of tret-butyl and 2 butoxyethyl alcohols and it is made the conclusion about existence in these solutions at various concentrations of two type local structure – clasters, enriched by water molecules and enriched by dissolved molecules. They obtained that the dimensions of these structures have larger values at $0.02 \prec x_1 \prec 0.20$ mole fraction of alcohols. It is obtained that dimensions of these clasters at 10^0C lower from critic temperature is about 50 Å.

Experimental. The Rayleigh isotropic light scattering was recorded at 90^0 scattering geometry with accuracy 5-6 %, the scattering volume was thermostated with accuracy $\pm 0.5^0$C. As standard liquid was used benzene for which, according to the work [7], value of scattering coefficient for wavelength 632.8 nm is $6.6*10^{-6}$ cm^{-1}. As a excited light source was the He-Ne gas laser. Chemically pure compounds and twice distilled water for study was used, all of which additionally were purify and undusted by distillation at low pressure.

The Raman spectra was recorded on difractional spectrometer DFS–52. As source of excitation was argon laser with λ=488 nm at power 1W. All measurements

was carried out at 90^0 geometry of scattering and at polarized exciting light. Polarized components of band were picked out by polarizing prism. The depolarizing wedge was used for the exception of spectrometer distorting influence. The spectral width of apparatus function in all experiments was 3.0 cm^{-1}. The experiments with solutions carried out at temperature 20^0C. The errors for determination of relative position of maxims and half width of bands were ± 0.3 cm^{-1}.

Results and discussion.

Not long ago we reported [8] the data of light scattering study in carboxylic acids+water mixtures, which were displayed on Fig. 1-3. It is seen that in acetic acid+water mixtures are observed two maxims of isotropic light scattering coefficient: at 0.06 and 0.12 mole fraction of acid. Was also displayed calculated, according formula (1) at f =1, dependence $R_c = f(x_1)$. Data for propionic and butyric acid were displayed on Fig.2 and 3, respectively. One can see that for propionic acid miximum of light scattering was observed at 0.02 mole fraction acid and for butyric acid mixtures was observed weak maximum at 0.05 mole fraction of acid on background of large usual concentrational scattering. With heating of these mixtures values of these maxima are decreased. The pattern here is similar to behavior of alcohol+water solutions [1], with increase of molecular weight of acid the maxims position displaced toward the lesser concentrations.

The cause of the arising these maxima in all above-mentioned mixtures, in our opinion, are the structural fluctuations as this was established for a additional isotropic light scattering maxima in some alcohol+water mixtures [1,7].

The second maximum of light scattering in acetic acid+water mixtures at 0.12 mole fraction of acid, most probably, was caused by usual heat fluctuations of concentration, as evidenced the calculated value of concentrational scattering (Fig.1, curve 3), which has a weak maximum at ~0.25 mole fraction of acid. Moreover both maxims in acetic acid+water mixtures decrease no equally in temperature range 20^0 – 60^0, firth 1.5, and second by 5 times.

What is the nature of these structural fluctuations in aqueous solution? At small acid composition in water as the result of acid molecules penetration in the water friable structure, without detectable disruption of local water structure, at certain concentration the friable structure of water is filled in and the breaking of considerable part of hydrogen bonds between water molecules is begun and a advantageous conditions for hydrate clatrates formation are created. As it was established in work [6] for aqueous solutions of tret-butyl and 2-butoxyethyl alcohols such clatrates may be enriched by both water and dissolved organic compound molecules.

Since the intermolecular hydrogen bond plays an important role in the breaking of water local structure and formation new structure, we decided to study of carboxylic acids+water mixtures by Raman spectroscopy on C=O vibrations band of acids in mixtures, as oxygen atom of this group must takes active participate in H-bond formation. Although the C=O vibration will is less sensible to structural fluctuations, but the C=O band will react to the formation or absence of H-bond. These data was displayed on Fig. 4-6. One can see (Fig.4) that in pure acetic acid in $I_{\parallel}(\nu)$ and $I_{\perp}(\nu)$ components of band are present three lines 1671, 1728 and 1762 cm^{-1} which correspond, according to literature data [10-13], to three molecular aggregations: 1671 cm^{-1} corresponds to the closed dimmers, 1728 cm^{-1} – to the open dimmers and open

polymer formations and 1762 cm^{-1} – to the molecular formations with free C=O group. Let us note that although in both $I_{\perp}(\nu)$ and $I_{\parallel}(\nu)$ components these three bands are observed, but its contributions in these two components are different. This means that these bands have different depolarization ratios. Any difference in frequencies of maxims for these three bonds do not noticed. This clearly shown on Fig.4 (curve 5), where was presented the dependence of depolarization ratio from frequency within C=O vibrations band. Further, in mixture of acetic acid with water the band intensity with intermediate frequency grows and at acetic acid content 0.5 mole fraction is observed the very broad asymmetric band on low-frequency side. With further dilution the low-frequency asymmetry disappears and even at acid content 0.12 mole fraction asymmetry is decreased, and at strong dilution is observed only one broad band with frequency 1717 cm^{-1}. (Fig.4, curve 3).

Thus, the strong dilution of acid by water leads to the availability of monotonous aggregated formations in which C=O band is appears included to H-bond formation. As judged from Raman spectra the transition to concentrations region where is observed the Rayleigh light scattering maxims means the transition from various aggregations of acetic acid to the formations only one type.

In solutions of propionic and butyric acid with water the Raman spectra of C=O vibrations band also confirm that at strong dilution in mixture exist only one type aggregations (Fig.5, curve 1 and Fig 6, curve 4), namely, open dimer and polymer formations with C=O groups included in H-bond formation completely.

In continuation of these experiments we studied the isotropic Rayleigh light scattering in aqueous solutions of trichloro-acetic acid and dimethylformamide. Obtained data were displayed on Fig. 7, 8. One can see that in both trichloro-acetic acid+water and dimethylformamide+water solutions at roam temperatures is observed one isotropic light scattering maximum at about 0.07 mole fraction of organic component in water. With the temperature growing the values of these maxima are decreased in first system by 1.5 times, and in second systems by 2 times. In dimethylformamide+water mixtures at temperature 80^0C, obviously, are displayed two maxims of isotropic light scattering which at 22^0C were not clearly seen (Fig.8, dotted curve). However to explain its origin for this system in the meanwhile it is difficult. The nature of these isotropic light scattering maxims, obviously, are also the structural fluctuations due to hydrate clatrates formation.

Conclusion.

All observed light scattering maxims are arranged at small maintain of dissolved in water organic substances. These maxims in light scattering are arising due to structural fluctuations of concentration in mixture. The cause of the origins of these structural fluctuations, in our opinion, following: at the dissolving of organic substance, molecules of which are able to form the hydrogen bonds with water molecules, the process of the dissolving in water takes place both through the penetrating of substance molecules in the cavities of friable water structure and through the bonding it by hydrogen bond with water molecules. At certain concentration the filling of cavities is finished and the processes of the destruction of water local structure and transition of the quasi-ordered structure to disordered one are started. At this time arise the favorable conditions for hydrate clatrate formation, and in mixture appear two type structurally differed small domains with water structure and with clatrate structure. In this moment at equilibrium between these structures the concentration fluctuations reach a large

values. With further dissolution the difference between these structures is decreased and mixture becomes more homogeneous. All these structural rebuildings in these solutions take place in very narrow interval of concentration, as a rule about $\Delta x \sim 0.05$ mole fraction. With the temperature increasing the development of structural fluctuation fall down.

References

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Fig 1. The isotropic Rayleigh light scattering in acetic acid+water mixtures: 1–20^0C; 2– 60^0C; 3 – calculated by formula (1) R_c values (dotted curve).

Fig 2. The isotropic Rayleigh light scattering in propionic acid+water mixtures: 1-20^0C; 2-80^0C.

Fig 3. The isotropic Rayleigh light scattering in butyric acid+water mixtures: 1-18^0C; 2-40^0C; 3-65^0C.

Fig 4. Raman spectra of C=O vibrations band for acetic acid and its solutions:1- $I_{\|}(\nu)$ pure acetic acid; 2- $I_{\perp}(\nu)$ pure acetic acid; 3- acetic acid+ water (0.12: 0.88 mole fr.); 4-acetic acid+CCl_4 (0.1: 0.9 mole fr.); 5-depolarisation ratio (right scale).

Fig 5. Raman spectra of C=O vibration band ($I_{\|}(\nu)$ component) for propionic acid and its mixtures with water: 1-0.10 mole fr of acid; 2-0.70 mole fr. of acid; 3-pure propionic acid.

Fig 6. Raman spectra of C=O vibration band of butyric acid+water mixtures: 1-0.90 mole fr; 2-0.50 mole fr.; 3- 0.10 mole fr.; 4-0.05 mole fr. of acid.

Fig 7. The isotropic Rayleigh light scattering in trichloro-acetic acid+water mixtures: 1-15^0C; 2-40^0C; 3-60^0C.

Fig 8. The isotropic Rayleigh light scattering in dimethylformamide+water mixtures: 1-22^0C; 2-80^0C.

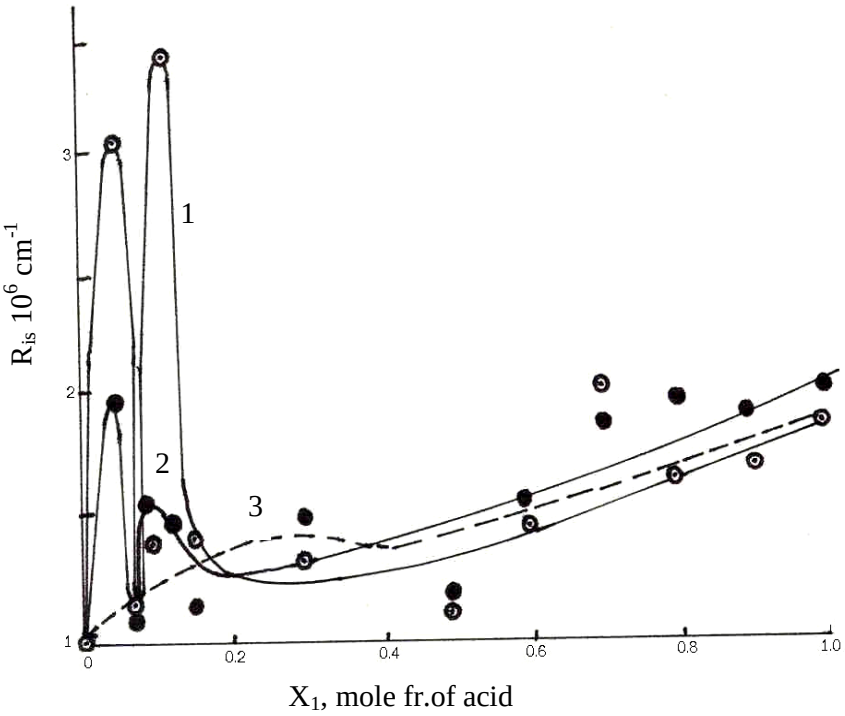


Fig.1.

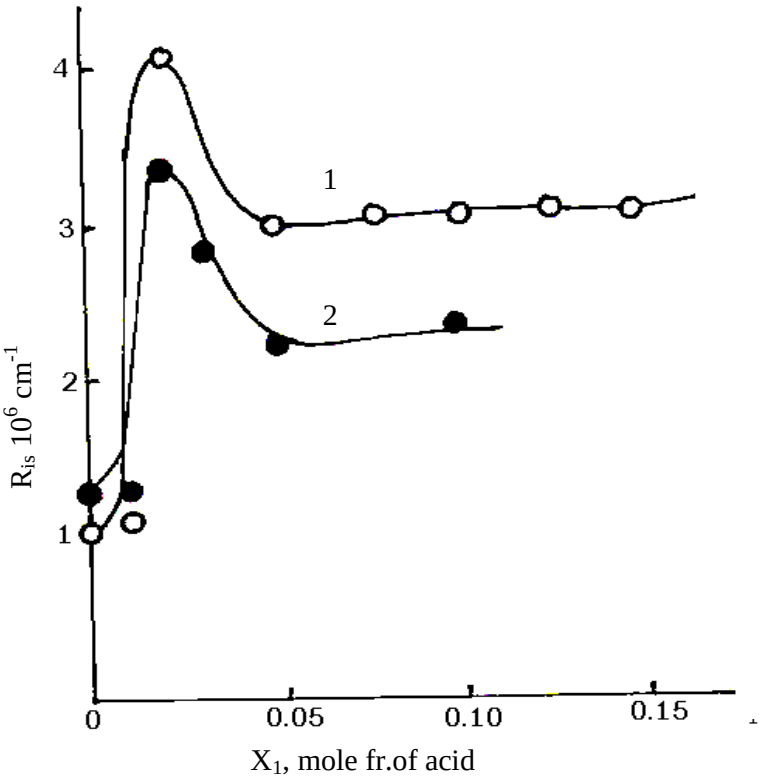


Fig.2.

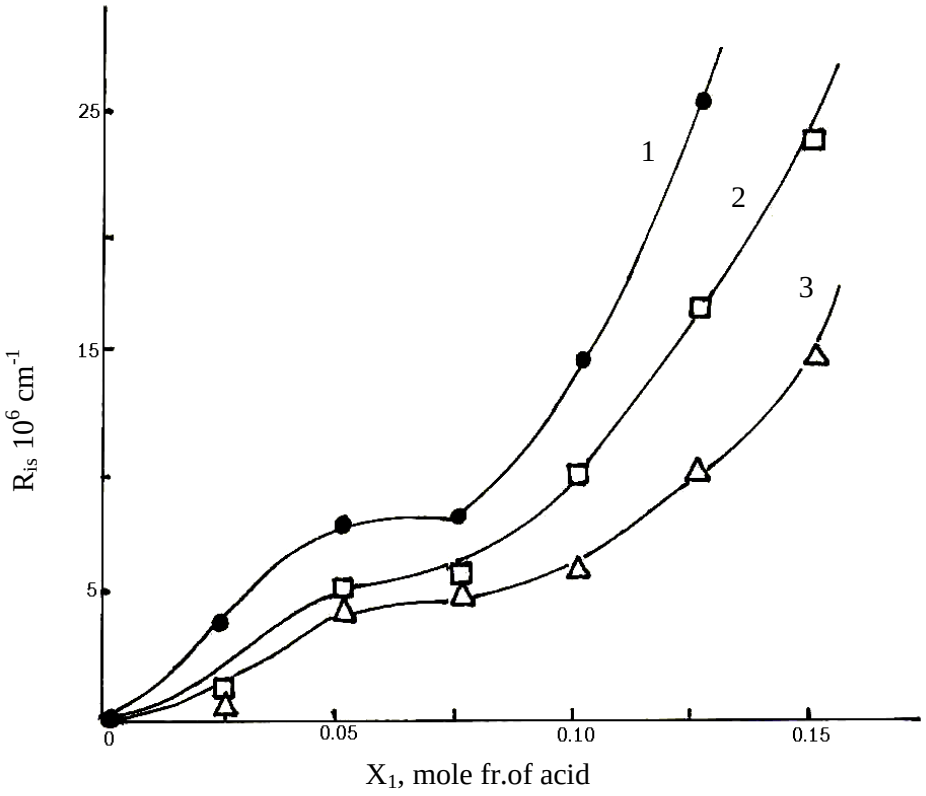
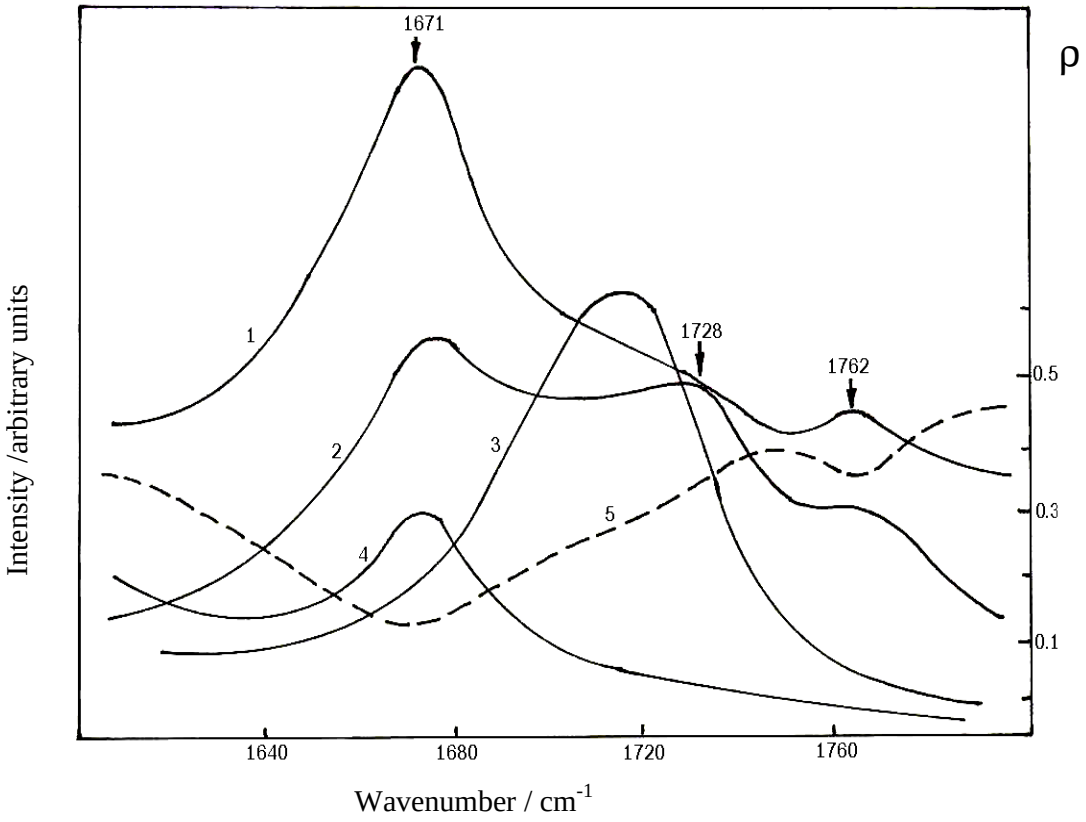


Fig.3.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1728
1762
ρ
0.5
0.3
0.1
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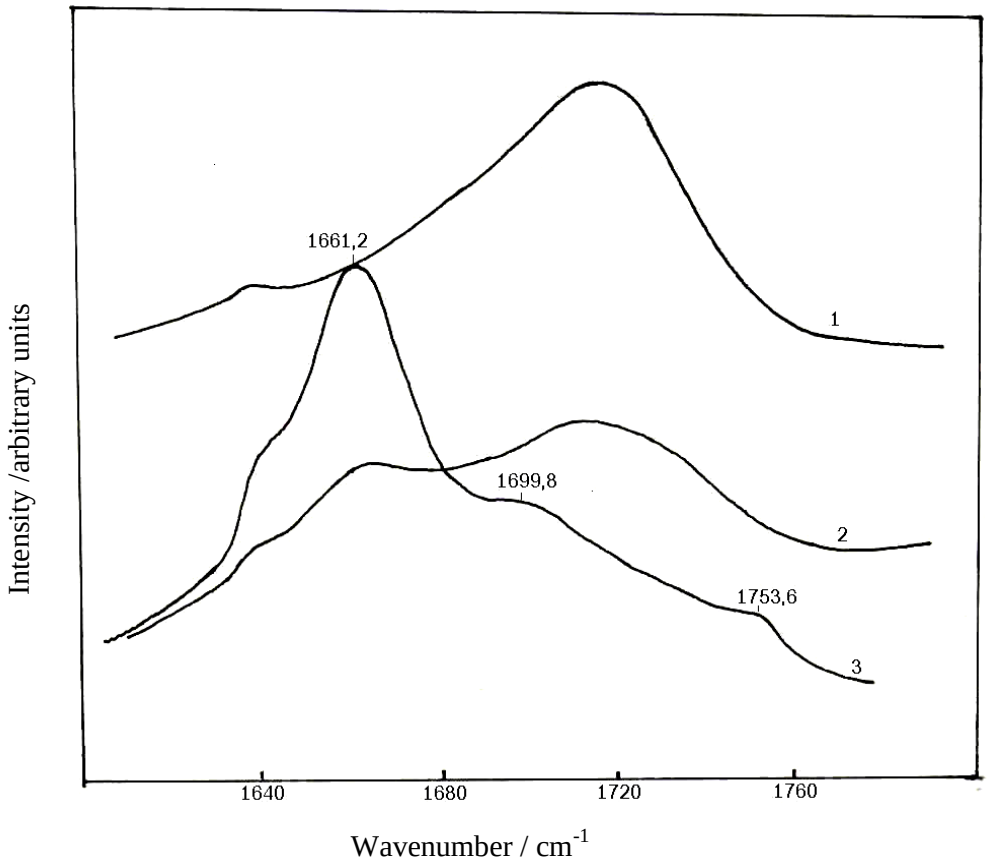
2
3
4
5
1640
1680
1720
1760
Intensity /arbitrary units
Wavenumber / cm-1

Fig.4.


Intensity /arbitrary units
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2
3
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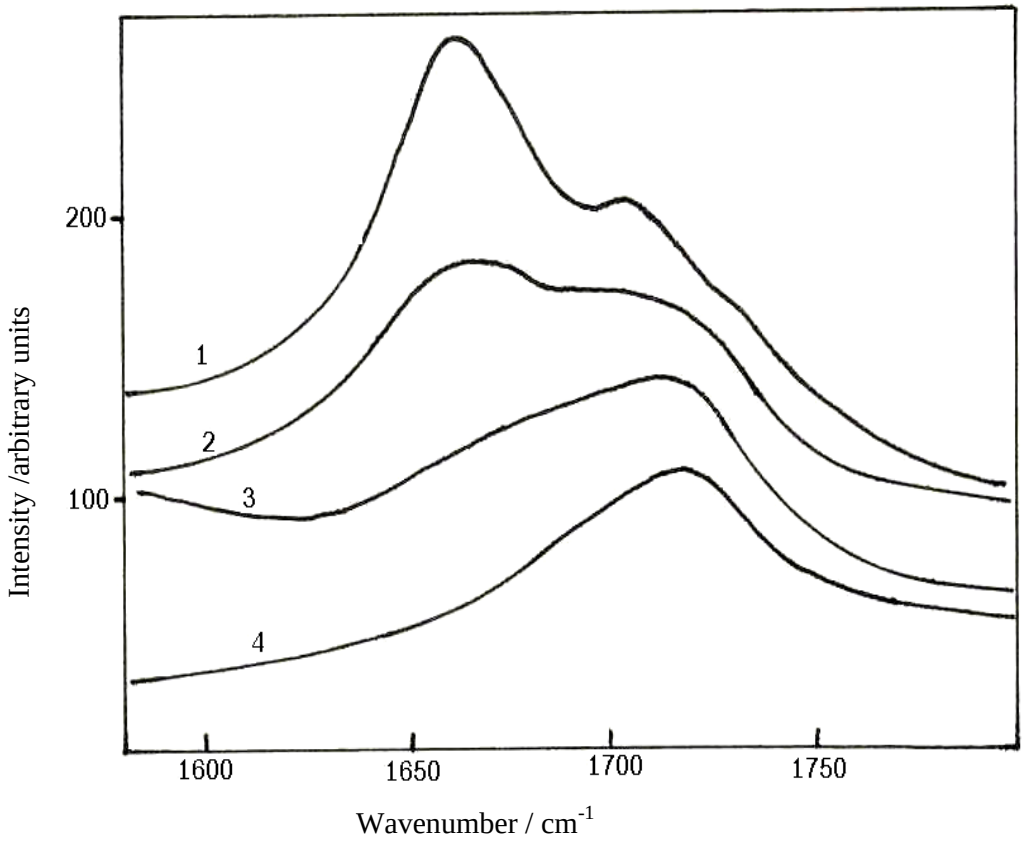
1680
1720
1760
Wavenumber / cm-1

Fig.5.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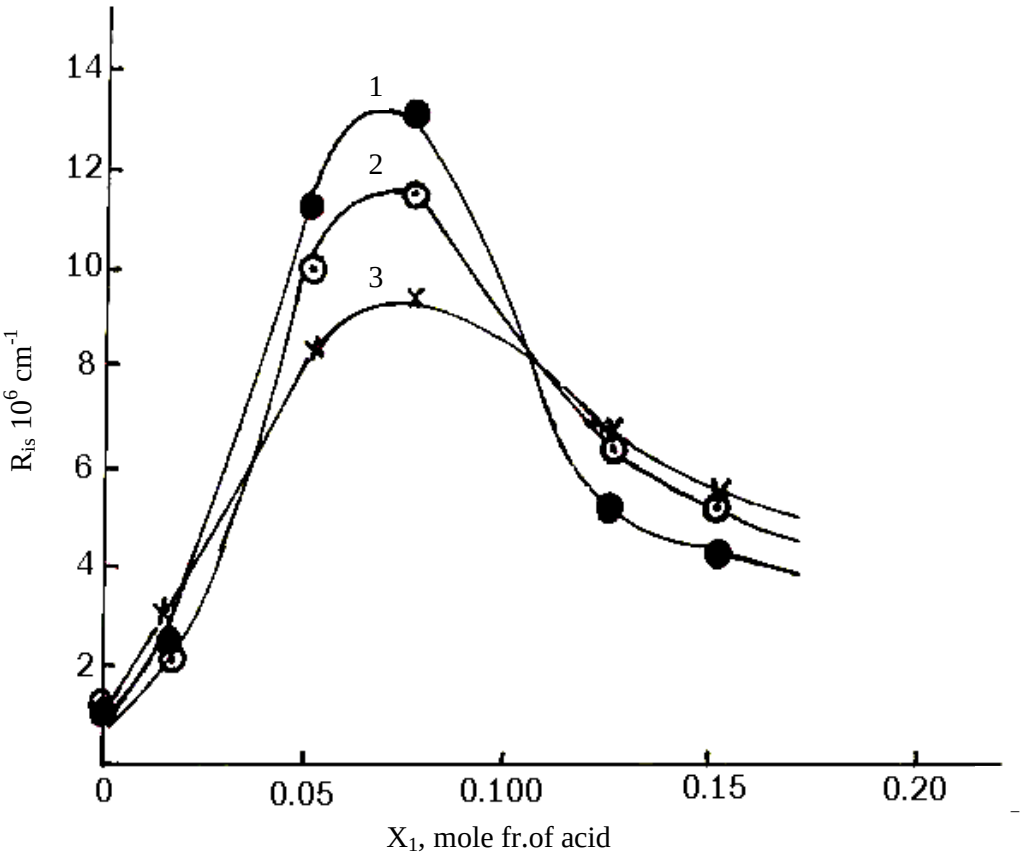
Wavenumber / cm-1

Fig.6.


14
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0.05
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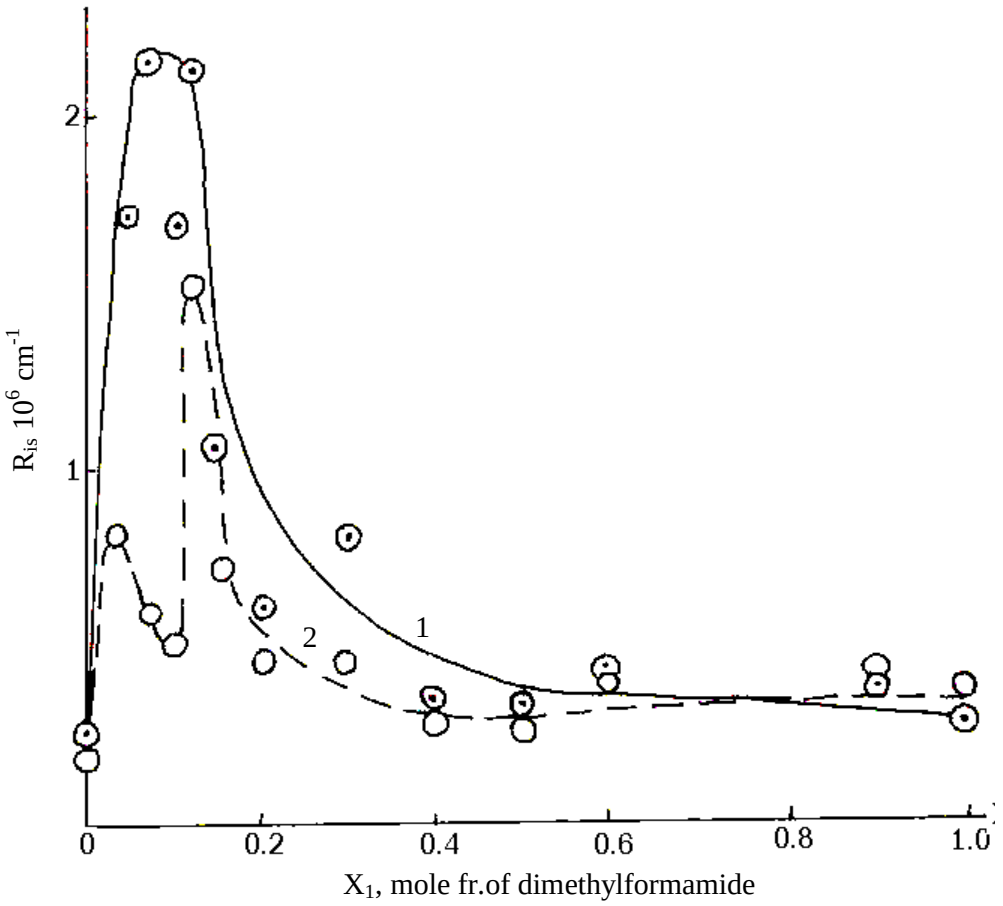
R_{is} 10^6 cm^{-1}
X_1, mole fr.of acid

Fig.7.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R_{is} 10^6 cm^{-1}
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0.2
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0.8
1.0
X_1, mole fr.of dimethylformamide

Fig.8.